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Ionization potential and nature of charge carriers in condensed hydrogen in wide pressure interval

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A simple model is used for estimation of the bottom energy of the electron conduction band V_0 and the forbidden gap energy E_g. It is shown that electrons in liquid hydrogens are localized not in the electron bubbles as it was considered previously but in molecular negative ions surrounded by empty voids of radius about 5 nm. The conductivity of fluid hydrogen at not too high pressures is connected to transfer of positively charged clusters and negatively charged bubbles. With increasing of pressure and density molecular dissociation occurs and electron localization on atoms becomes more favorable, also with creation of void around atomic negative ion. At high enough concentration of atoms a probability of the tunnel transition of an electron from one atom to another becomes closed to the unity, the energy level of the negative ion degenerates in the band, and the conductivity is caused by the transfer of these quasifree electrons. It is supposed that this mechanism of the charge transfer may play important role in region of the fluid hydrogen metallization.

KEYWORDS：Hydrogen, High Pressure, Conductivity, Ionization Potential, Bubble, Liquid

凝縮状態における水素の広い圧力範囲での電離ポテンシャルとキャリアの性質

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液体水素中においては電子はこれまで考えられていたように電子バブルを作って局在化しているのではなく、分子性負イオンとなって周りをボイドで囲まれた状態にある。液体水素中の電気伝導は余り高圧でないときには正電荷のクラスターとバブルをともなう分子性負イオンの移動で説明される。圧力と密度が高くなるにつれて分子の解離が起こり電子は原子に局在化した原子状負イオンとなり周りをボイドが囲む形となる。充分に高密度となると電子の原子から原子へのトンネル確率が１に近くなり、負イオンのエネルギー準位が縮退し電気伝導は準自由状態の電子のトランスファによって生じる。このメカニズムが流体水素の金属化においても重要な役割を演ずる。

1. Introduction

Investigations of hydrogens behaviour in solid, liquid, and plasma state are of significant importance from both scientific and technological viewpoint. Importance for astrophysics follows from the fact that hydrogen is the most abundant chemical element, which constitutes about 3/4 of the Universe matter. Jupiter and Saturn together contain over 400 Earth masses, most of which is hydrogen, heated and compressed to high temperatures and pressures. Hydrogen is fluid at these conditions. The convective motion of electrically conducting hydrogen produces magnetic field of giant planets by the dynamo action (see [1] and references therein). Knowledge of the equation of state and physical properties of hydrogen and its isotopes is very important for successful solution of the problem of the inertial nuclear fusion. Intriguing possibility of metastable metallic and even superconducting phases of solid hydrogen at ambient pressure has been predicted.[2] Liquid hydrogen is presently used as a rocket fuel and is predestined for supersonic and hypersonic space vehicles. It is considered as effective coolant of normal and superconducting machines, and as perspective fuel for land-based transport. Storage of high density hydrogen in storage materials such as metals and metal alloys is one of the most important technological problems to be solved to increase the effectiveness of hydrogen fuel cells.[3] Liquid hydrogen favorable characteristics include its high heating value per unit mass, its wide ignition range in hydrogen/oxygen or air mixtures, as well its large flame speed and cooling capacity due to its high specific heat.

Wigner and Huntington in 1935 predicted that molecular diatomic hydrogen would undergo a transition to a metallic state at an imposed pressure of about 25 GPa.[4] Current predictions are in a range close to 300 GPa.[5] But despite an unrelenting experimental assault, dense solid hydrogen shows no evidence of metallic behaviour.[6] In the fluid, electrical conductivity measurements under multiple-shock compression indicate that hydrogen becomes metallic at pressures about 140 GPa, ninefold initial fluid density, and temperature about 3000 K.[7-10] Electrical conductivity has also been measured under single-shock compression up to 20 Gpa and 4600 K.[11] Those experiments show that conductivity is thermally activated similar to the semiconducting fluid and it becomes greater than 1 $(\Omega\cdot\mathrm{cm})^{-1}$at 200 GPa and 400 K. The pressure dependence of the conductivity measured in Ref. (9) is shown in Fig. 1. The change in slope at 140 GPa is indicative of the transition to the metallic state. An analysis of the measurements in the range 93-120 (semiconducting regime) resulted in the equation typical for liquid semiconductors

$$\sigma = \sigma_0 \exp\left[-E_g(\rho)/2k_BT\right], \qquad (1)$$

where σ is electrical conductivity, σ_0 weakly depends on density ρ, $E_g(\rho)$ is the density-dependent electron band gap of the fluid, k_B is the Boltzmann's constant, and T is temperature. If temperature dependence of conductivity is connected with transition of electrons from the ground state to the continuous spectrum, then E_g coincides with ionization potential of the hydrogen molecule in the matter. The results of the least squares fit of the experimental data to Eq. 1 are

$$\begin{gathered} E_g(\rho) = 1.22 - 62.6\cdot(\rho - 0.30) \\ \sigma_0 = 90 \\ 0.29 \le \rho \le 0.30, \end{gathered} \qquad (2)$$

where $E_g(\rho)$ is in eV, ρ is in $\mathrm{mol/cm^3}$, and σ_0 is in $(\Omega\cdot\mathrm{cm})^{-1}$. Note that a value 200-300 $(\Omega\cdot\mathrm{cm})^{-1}$ is typical for liquid semiconductors.[12] The band gap was also estimated as E_g = 11.7±1.7 eV at the point ρ = 0.13±0.005 $\mathrm{mol/cm^3}$ in the single-shock experiments.[11] Metallization density is defined to be that at which the mobility band gap E_g is reduced by pressure to $E_g \sim k_BT$, at which point

E_g is filled in by fluid disorder and thermal smearing. The $E_g(\rho) \approx k_B T$ at density of about 0.32 mol/cm^3 and temperature of about 2600 K (0.22 eV). Thus fluid hydrogen becomes metallic at about 140 GPa and 2600 K via continuous transition from a semiconducting to metallic fluid.

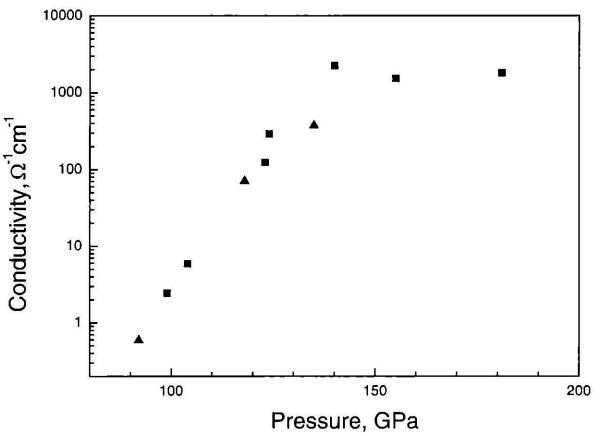

Fig.1. Electrical resistivity of H_2 and D_2 as a function of pressure.[9] Slope change at 140 GPa is transition from semiconducting to metallic fluid.

The band gap E_g has been measured only at solid H_2 and D_2 at low temperatures (about 5 K) and low (saturation) pressures.[13, 14] The vacuum ultraviolet absorption spectra of these two hydrogen isotopes are practically identical. The low energy component of the spectra below 15 eV was assigned to the Wannier exciton transitions. From analysis of the high members of the Wannier series given in Ref. (14) it follows that in hydrogen $E_g \approx 14.7$ eV and in deuterium $E_g \approx 14.9$ eV. These values are close to the gas phase ionization potentials of the hydrogen molecules: $I_g = 15.43$ eV for H_2 and $I_g = 15.47$ for D_2. Knowledge of E_g permits to estimate the energy of the bottom of the electron conduction band V_0. In fact, the molecular ionization potential in a dielectric matter is related to the gas phase ionization potential by

$$E_g = I_g + P_+ + V_0, \qquad (3)$$

where P_+ is the polarization energy of the medium by positive ion. For estimation of the value of P_+ Born formula can be used

$$P_+ = -\frac{e^2}{2R_i}\left(1-\frac{1}{\varepsilon}\right) \qquad (4)$$

Here R_i is the radius of the cavity where a point charge resides surrounded by a homogeneous liquid or solid with the dielectric constant ε. Usually, R_i is chosen equal to the crystallographic ionic radii or to the hard core radii of the neutral parent molecule. Good agreement with results of the theoretical estimates of P_+ advanced for solid rare gases[15, 16] may be achieved for

$$R_i = R_s, \quad R_s = (3/4\pi N)^{1/3} \qquad (5)$$

where R_s is radius of the cell occupied by a molecule in the medium with concentration of the molecules N. Substitution Eq. 5 into Eq. 4 gives $P_+ = 0.7$ eV for H_2 and $P_+ = 0.8$ eV for D_2. Thus the energy of the bottom of the electron conduction band V_0 is approximately equal to –0.05 eV in solid H_2 and +0.20 eV in solid D_2.

A sign and value of V_0 are determined by competition between polarization and exchange interaction of an electron with molecules of the medium

$$V_0 = T_e + P_e, \qquad (6)$$

where $P_e < 0$ is the polarization energy of the medium by electron and $T_e > 0$ is the minimum kinetic energy which free electron can have in a system of short-range repulsive scatters. With decreasing N relative contribution of the polarization interaction increases and thus in liquid and gas phases of the hydrogen V_0 has to be also negative. In the ideal gas the optical model[17] may be used for estimation of V_0

$$V_0 = \frac{2\pi\eta^2}{m} LN, \qquad (7)$$

where m is the electron mass and L is the electron-molecule scattering length. This implies that L has to be negative and demonstrate a Ramsauer-Tawnsend minimum. The scattering length was obtained in spectroscopic investigation of properties of

electrons localized above the surface of the solid hydrogen.[18, 19] The resonant energy of electron transition between ground and excited surface states was found in this experiment to depend on density N of the H_2 molecules in the vapor phase. The linear density shift of the energy shown in Fig. 2 was interpreted in terms of the optical model (in full analogy with Fermi shift of energy of high excited Rydberg atoms in a gas atmosphere) by means of Eq. 7. This gave the value $L = -0.14 \pm 0.04$ nm and negative V_0 what is in qualitative agreement with previously discussed results of spectroscopic investigations of solid hydrogen. Note that currently accepted value $L = +0.067$ nm. Discussion of possible reasons of this discrepancy one can find in Ref. 19.

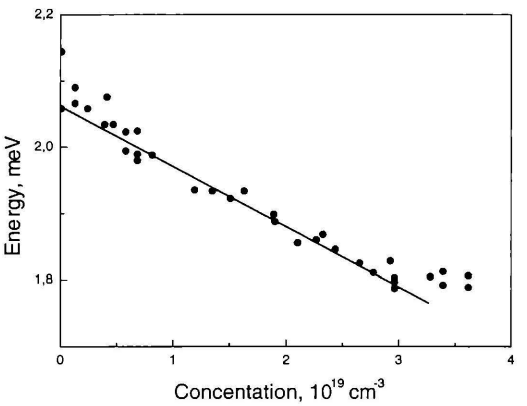

Fig.2. Frequency of the surface electron 1→2 transition as a function of density of hydrogen molecules in gas phase.[19]

Negative value V_0 points out the absence of the potential barrier for penetration of an electron from the gas phase to bulk liquid or solid hydrogen. At first sight this contradicts to a number of well-known experimental facts. First, the possibility of the electron localizationv above the surface of condensed He, Ne, and H_2 is usually connected with existence of the potential barrier for electrons at the surface of these three matters having small polarizability of atoms or molecules.[20, 21] Second, in experiments on mobility of charge carriers in liquid[22-24] and solid[25-27] hydrogens very low mobility of negative charges of the same order or in some cases even less the mobility of positive charges was observed. Current interpretation of this effect supposes that just as in liquid and solid helium, the positive charges are clusters (Atkins' snowballs)[28] consisting of a positively charged molecular ion surrounded by a layer of neutral molecules and negative charges in condensed hydrogens are electrons localized in bubbles or voids of several atomic sizes.[21] This interpretation also implies an existence of the sizable potential barrier of about 1-2 eV at the surface of the electron bubble. Third, irradiated solid hydrogens display a number interesting spectral features. Hydrogen mixtures containing tritium, when cooled below about 10 K, showed additional lines in the fundamental absorption spectrum.[29] The new lines were interpret as Stark-shifted molecular transitions which appearance was caused by the presence of trapped charges of both sign in the lattice as result of the ionizing tritium radioactivity. Proton- and γ-irradiated samples show the same features. Analysis of Stark shifts resulted to conclusion that two species of each charge exist, one mobile and one less mobile. Each of the less mobile charge species is responsible for induced absorption features. The mobile negative charge is thought to be a small polaron and its immobile counterpart an electron trapped in the form of a bubble.[30] In addition to the Stark-shifted features a number of spectral features also attributed to trapped electrons have been observed in irradiated solid hydrogens (see, for example, Ref. 31 and references therein). A simple square-well model for the electron bubble gives a good fit to the observed spectra only for an unreasonably large well depth $V_0 = 3.8$ eV.[32]

One of the aims of the present work is to eliminate aforementioned contradictions between different experiments. With help of a simple model we show that even in the case of negative V_0 (but not very large in the absolute value) two dimensional electron surface states may exist owing to the additional potential barrier at the surface which appearance is connected to the different range of polarization

and exchange forces. Important role of the polarization energy at the surface and interface was also reported for other dielectric and semiconducting systems.[33] Using the fact of recently observed formation of the ion H_2^- in solid hydrogens,[34-36] we conjecture that the low mobility of negative charges in condensed hydrogens is a result of the electron capture by hydrogen molecule and bubble creation around it but not result of the electron bubble creation. We assume that in the case of irradiated liquid and solid hydrogens availability of admixture of hydrogen or deuterium atoms is decisive and electrons are localized In H^- surrounded by empty void of smaller size than in the case of H_2^- Near metallization pressure of hydrogen considerable dissociation of H_2 (about 10%) takes place.[9] Electrons are localized in H^-. With increasing pressure overlapping of the neighboring negative ion states should result in formation of the extended electron band and lead to the insulator-metal transition. In this paper results of our determination of the density dependence of V_0 and E_g are presented and compared with results of the single-shock experiments.

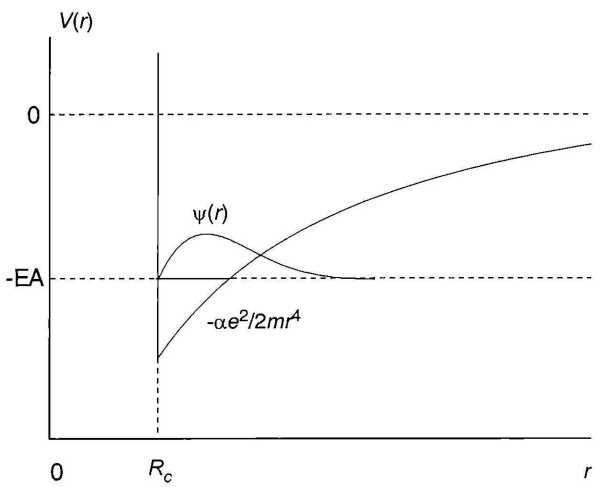

Fig.3. potential for the electron-atom or electron molecule interaction $V(r)$ and the electron wave function in the negative ion$\psi(r)$

2. Energy of the bottom of the electron conduction band

In dense fluids and solids the interaction between atoms and molecules plays important role, optical model (7) is inapplicable for estimation of V_0, and more detail consideration of Eq. (6) is necessary. The energy of polarization interaction of electrons with a matter P_e differs from the ion polarization energy P_+. Calculation fulfilled for solid rare gases[16] are well fitted by

$$P_+ = -\frac{1}{a}\varphi_+\left(\frac{\alpha}{a^3}\right), \qquad \varphi_+(t) = \frac{3.154t - 3.860t^2}{1 + 2.55t - 4.750t^2} \tag{8}$$

$$P_e = -\frac{1}{a}\varphi_e\left(\frac{\alpha}{a^3}\right), \qquad \varphi_e(t) = \frac{4.966t + 0.924t^2}{1 + 3.244t + 0.957t^2} \tag{9}$$

where $a \cong 1.2R_s$ and t satisfied the conditions $0 < t < 0.2$. The approximation (8) coincides numerically with the calculation data of Ref. (15) and Born formulae (4). Well known that in the case of helium isotopes and other rare gases the value of V_0 depends essentially on the atomic density and is practically independent of isotope composition, aggregative state and type of the crystal structure.[37] Therefore there is good reason to believe that Eqs. (8) and (9) can be used for solid and fluid hydrogen and deuterium. Results of estimation of the polarization energy of positive ions and electrons near the triple point of H_2 and D_2 are listed in Table 1.

Table1 Results of estimation of characteristic energies of H_2 and D_2 near their triple points: positive ion P_+ and electron $P_e$polarization energy, minimum electron kinetic energy T_e, energy of the bottom of the electron conduction band V_0, and electron mobility gap or ionization potential E_g. All values are in eV.

	Hydrogen		Deuterium	
	Liquid	Solid	Liquid	Solid
P_+	-0.67	-0.78	-0.78	-0.91
P_e	-1.08	-1.26	-1.26	-1.48
T_e	0.95	1.09	1.09	1.27
V_0	-0.08	-0.16	-0.16	-0.18
E_g	14.68	14.49	14.53	14.38

For estimation of the minimum electron kinetic energy T_e it is necessary to concretize the short range part of the interaction potential. The interaction of an electron with atom or molecule in vacuum can be qualitatively described by means a simple model potential shown in Fig. 3.[38, 39]

$$V(r) = \begin{cases} \infty, & r \le R_c \\ -\dfrac{\alpha e^2}{2mr^4}, & r > R_c \end{cases} \qquad (10)$$

Here α is the atomic or molecular polarizability. The only parameter of the potential, which is the solid core radius Rc, is fitted as follows. In the case, when a stable negative ion of the corresponding species exists (as it is in the case of H^-), such Rc is looked for with which the solution of the Schrödinger equation with potential (10) gives a correct value of the electron affinity EA. The atomic hydrogen has EA = 0.754 eV[40] what results in R_c = 0.032 nm. Negative ion of the molecular hydrogen does not exist in the vacuum. In this case, it is possible to use known connection between R_c, α and the electron scattering length L[41]

$$L = \sqrt{\frac{\alpha}{a_0}} \cot \sqrt{\frac{\alpha}{a_0 R_c^2}}, \qquad (11)$$

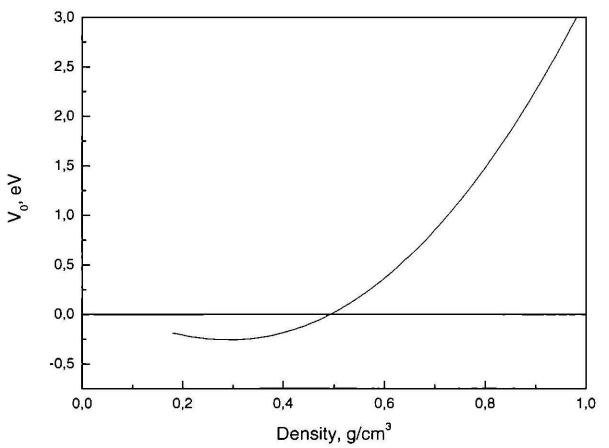

Fig.4. Energy of the bottom of the conduction band V_0 in fluid D_2 as a function of densityρ.

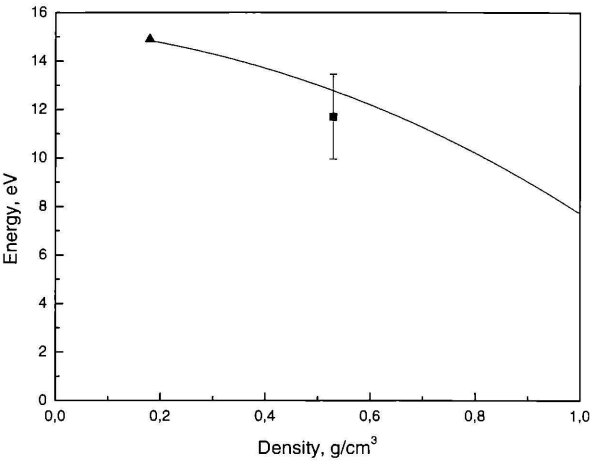

Fig.5. Electron forbidden gap energy in fluid D_2 as a function of density ρ.

where a_0 is the Bohr radius. Substitution in Eq. (11) the value L = –0.14 nm results in R_c = 0.052 nm. This value of R_c seems quite reasonable because of scattering at two closed atoms it has to be twice as atomic R_c but correlation in positions of atoms in the molecule reduces slightly the value of R_c.

Knowing the radius of the molecular hard core, it is possible to calculate the value of zero point electron energy T_e. An approach usually used for this is based on the Wigner-Seitz model.[15, 37, 42] In this model the medium is divided into equivalent spheres of radius R_s. Each sphere contains a hard core of radius R_c in its center. A free electron may be in any cell with equal probabilities. Therefore the electron wave function $\Psi(r) \sim r^{-1}\sin[k(r-R_c)]$ and $\Psi'(r)$ have to be continuous at the cell boundaries what is possible only if $\Psi'(R_s)=0$. This gives

$$T_e = \frac{\eta^2 k^2}{2m}, \qquad (12)$$
$$kR_s = \tan[k(R_s - R_c)].$$

Results of estimations of T_e, and following from Eqs. (6) and (3) values of V_0 and E_g, are also listed in Table 1. One can see that our estimation of the ionization potential E_g in solid hydrogens is in a good agreement with spectroscopic measurement[15] and the bottom of the electron conduction band V_0 is negative in all considered cases.

Given model permits to determine dependence of V_0 and E_g on the fluid density ρ. Results of our calculations are shown in Figs. 4 and 5. V_0 has a minimum at density about 0.3 g/cm^3 and becomes positive at about 0.5 g/cm^3. Such behavior is typical for all fluid rare gases having negative V_0 at ambient conditions. The forbidden gap energy decrease with density and in limits of the experimental errors coincides with E_g produced by single-shock compression at the point 0.53 g/cm^3.

3. Surface potential barrier and localization of electrons on hydrogen surface

For liquids with positive value of V_0 (for example, helium and neon) electron transfer from the vacuum into the liquid is hampered by this barrier. An electron approaching the surface from the vacuum will feel, nevertheless the influence of its positive image charge inside the liquid. The potential of this attractive image force above the surface is given by

$$V(z) = -\frac{Qe^2}{z}, \quad Q = \frac{(\varepsilon - 1)}{4(\varepsilon + 1)} \qquad (13)$$

where z denotes the coordinate perpendicular to the surface and ε is the dielectric constant of the matter. The attraction by the image force and barrier given by V_0 lead to a bound surface states.[20, 21] The electron is, however, still partially frees to move along the surface and has high mobility in these directions. In the case of liquid helium potential barrier $V_0 \sim 1$ eV is high in comparison with the binding energy of the localized electron. Therefore it is possible to put with a good accuracy $V_0 = \infty$ and to take into account the presence of interface by the boundary condition of the wave function $\Psi|_{Z=0}=0$. In this case the attractive potential gives rise to hydrogenlike wave function with Bohr radius becoming a_0/Q. The energy levels correspond to the Rydberg series and electron energy spectrum is given by

$$E_n(\mathbf{k}) = \frac{\eta^2 \mathbf{k}^2}{2m} + \frac{mQ^2e^4}{2\eta^2 n^2}, \quad n = 1,2,.... \qquad (14)$$

where $\mathbf{k}$ is a two-dimensional wave vector of the electron parallel to the helium surface. Owing to small polarizability of helium ($Q \cong 1/144$) the ground state binding energy is also small ($E_1(0) \cong .7.5$ K $<< V_0$) and assumption $V_0 = \infty$ is quite reasonable in this particular case. The electron is localized at the distance order of 100 nm from the surface and thereby the true behavior of the interaction potential at the distance order of interatomic from the surface is not very important. Frequencies of the 1-2 and 1-3 transitions correspond to 125.9 and 148.6 GHz, respectively.

In the case of condensed hydrogens situation is different. As we shown above, V_0 is negative in both liquid and solid hydrogens and at first sight the surface electron localization is impossible. Nevertheless such states were observed.[18, 19, 43, 44] Dwell in more detail on the spectroscopic measurements with surface electrons on solid hydrogens surfaces.[19] The tunable laser source enabled to observe the photoresonance of the surface electrons when changing the potential of the lower electrode U (and, consequently, the confining electric field E) altered the electron spectrum. The photoresonance signal amplitude depended linearly on the laser intensity and on the surface charge density. The transition frequency in the limit of zero electric field E and hydrogen gas pressure P was equal to 3.15±0.05 THz. As in the case of similar experiments for electrons over ^{3}He and ^{4}He,[45, 46] the energy spectrum can be approximated by introducing the Rydberg correction δ

$$E_n(0) = \frac{mQ^2e^4}{2\eta^2 (n+\delta)^2}, \qquad (15)$$

where δ is independent of n. Measurements of δ for $_3$He and $_4$He gave –0.014 and –0.022, respectively, while for solid hydrogen δ = –0.11 was obtained.[18, 19] As we already

mentioned, Zavyalov and Smolyaninov found out that for electrons over solid hydrogen and deuterium the transition frequencies depend strongly on the vapor density. Analysis of this dependence allowed determining the scattering length L that we use in our estimations. Negativity of the scattering length is important evidence of negativity of V_0.

To understand why creation of the localized surface states is possible in the case of negative V_0, let us consider in more detail the interaction of an electron with the hydrogen surface. The interaction potential $V(z)$ is shown schematically in Fig. 6. Inside condensed hydrogen the potential energy of the long-range polarization interaction P_e is determined, for example, by Eq. 9. Approaching the surface P_e increases. At the surface it is tied continuously to the image force potential, which far from the surface is determined by Eq. 13. An electron located just at the sur-face interacts with a half of molecules with which it interacts in the bulk matter. Thus it is reasonable to suggest that at the surface the polarization energy is approximately equal $P_e/2$. In addition to the polarization interaction there is the short-range exchange interaction of the electron with electrons of hydrogen molecules, which results in the shift of the minimum electron energy V_0 by positive value T_e. Dependence of $T_e(z)$ is significantly more abrupt than of $P_e(z)$. We approximate it by step function. Resulting surface potential depicted in Fig. 6 by solid line represents potential barrier for penetrating of electrons from the vacuum side. It is obvious that if V_0 is not too small the surface electron localized states may exist.

For determination of the surface electron energy spectrum we use even more simple potential. Outside hydrogen it coincides with the image force potential (13) down to $z = R_c$ = 0.052 nm. At shorter distances the potential is considered to be constant, $V(z) = V(R_c)$. Inside hydrogen the potential is also considered to be constant, $V(z) = V_0 - P_e/2$. Solution of the Schrödinger equation gives the spectrum Eq. 15 with $\delta \cong -0.2$ that is practically independent of n. For so simplified model the agreement with the experimental value $\delta = -0.11$ is quite satisfactory. Worthwhile to note that we used following continuity conditions for the electron wave function $\phi(z)$[47]:

$$\psi(-0) = \psi(+0), \qquad m_{eff}^{-1}\psi'(-0) = m^{-1}\psi'(+0) \tag{16}$$

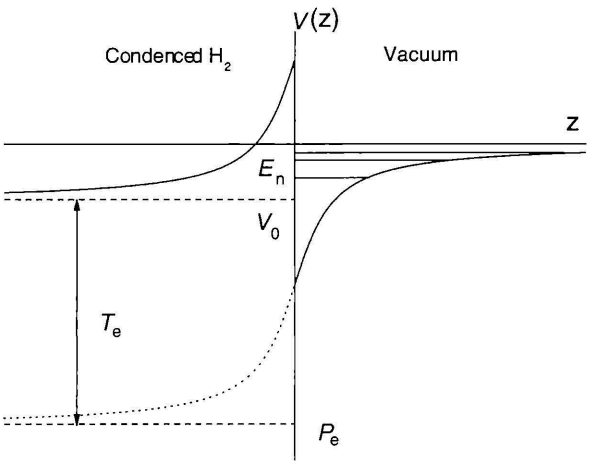

Fig.6. Schematic arrangement of the electron interaction potential at the surface of condensed hydrogen.

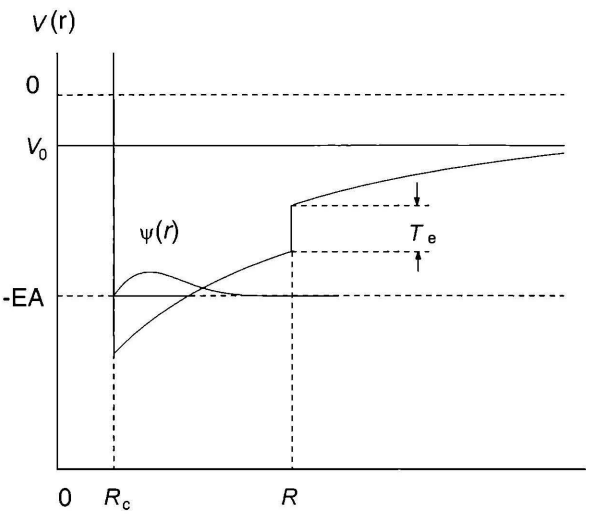

Fig.7. Model potential for the electron-atom or electron molecule interaction $V(r)$ and the electron wave function in the negative ion$\psi(r)$ inside a bubble of radius R

where m_{eff} is the electron effective mass. In liquid helium $m_{eff} \cong m$ and both masses are

canceled in Eq. 16. In solid hydrogen $m_{eff} \cong 0.2m$. The sudden change of the electron effective mass at the hydrogen surface results in significant increase of the surface electron binding energy.

4. tructure and energy spectrum of atomic and molecular negative ions in condensed hydrogens

The electron affinity to atoms and molecules increases in condense dielectrics in comparison with its values in vacuum.[48-51] As result of irradiation or thermal dissociation some amount of atomic hydrogen may be present in condensed molecular hydrogen. Thus we perform our estimations both for atomic and molecular negative ions. At the moment of the electron transition to the level of negative ion surrounding matter can be considered as undisturbed. In this case the electron binding energy in the negative ion may be estimated from solution of the Schrödinger equation with a potential slightly different from Eq. 10 and Fig. 5. It is represented in Fig. 7. At the surface of the void surrounded negative ion with $R = R_s$ the interaction potential varies stepwise by the value T_e. The estimation of the electron binding energy gives, for example, for H^- in liquid hydrogen at the triple point EA $\cong$ 1.33 eV, and for D^- in solid deuterium also at the triple point EA $\cong$ 1.42 eV. A continuous red emission spectrum was observed during proton-beam irradiation of solid D_2 and H_2 maximizing near 830 nm (1.49 eV).[31, 52] We believe that the electron attachment to D and H is responsible for this emission. Similar estimation shows that the electron affinity to the hydrogen molecule in undisturbed hydrogens is negative. Thus the radiative formation of ionsH_2^- and D_2^- is impossible. With increasing fluid density the electron binding energy increased. Results of our calculation of the electron affinity to the atomic deuterium in fluid molecular deuterium are shown in Fig. 8. At the same densities the bound state of molecular negative ion D_2^- does not exist.

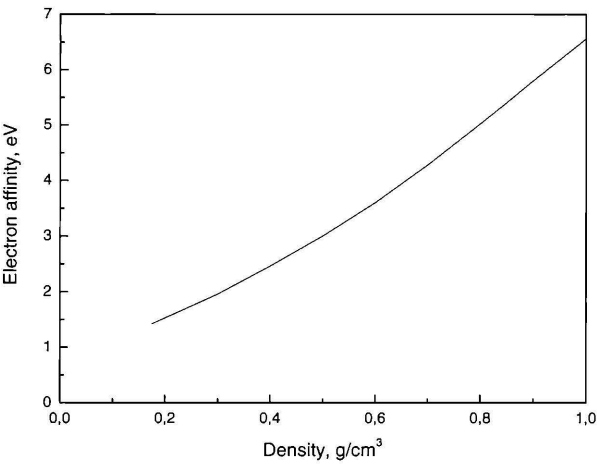

Fig.8. Electron affinity to the atomic deuterium in fluid deuterium as function of density

After the atomic negative ion formation interaction of the outer electron with surrounding matter results in creation of a void around the ion. At that the electron energy decreased. At bubble radius about 0.5 nm the electron energy shift is about 0.15 – 0.20 eV. With accounting of the potential barrier at the surface of void, which is of order of $P_e/2$, the electron detachment energy is equal approximately to 1.9 eV for H^- in liquid H_2 and 2.2 eV for D^- in solid D_2. The last value is somewhat different from the experimentally measured value of the electron bound-free transition energy in the proton-irradiated solid deuterium equal to about 3.1 eV.[53] Nevertheless we consider that photodetachment of electrons from ions D^- may be responsible for this ultraviolet absorption spectrum and suppose that more refine calculation of hydrogen negative ion spectrum is capable to improve agreement with experiment. Creation of negative ions H_2^- and D_2^- becomes also possible inside voids of sufficiently large radius. For example, the electron detachment energy for ion D_2^- in the void of diameter 0.5 nm in solid D_2 is equal about 1.3 eV. Close values are valid for H_2^- in liquid and solid H_2, and for D_2^- in liquid D_2. This allows as to suppose that low mobility of

negative charges in liquid and solid hydrogens is connected with its localization in molecular or atomic (when dissociation of molecules takes place) negative ions surrounded by a bubbles or voids.

5. Conclusion

A simple model for estimation of the bottom energy of the electron conduction band V_0 and the forbidden gap energy E_g was proposed rested on the experimental investigation of the exciton absorption spectrum in condensed hydrogens. Estimation of E_g is in a good agreement with values obtained in the measurements of conductivity by single-shock wave experiments. It was shown that electrons in liquid hydrogens are localized not in the electron bubbles as it was considered previously but in molecular negative ions surrounded by empty voids of radius about 5 nm. The conductivity of fluid hydrogen at not too high pressures is connected to transfer of heavy complexes – positively charged clusters and negatively charged bubbles. With increasing of pressure and density molecular dissociation occurs and electron localization on atoms becomes more favorable, also with creation of void around atomic negative ion. At high enough concentration of atoms a probability of the tunnel transition of an electron from one atom to another becomes closed to the unity, the energy level of the negative ion degenerates in the band, and the conductivity is caused by the transfer of these quasifree electrons. This mechanism of the charge transfer may play important role in region of the fluid hydrogen metallization.

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